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Evolution of heat during precipitation in lead-tin alloys

By Josef Nyström

With 5 figures in the text

§ 1. Introduction

During the last few years some calorimetric measurements during transformations in alloys have been carried out under the direction of Professor Borelius (1, 2, 3). The previously used method has been successful in many cases, but sometimes the transformations are too rapid for measurements of this kind. This investigation is an attempt to make measurements during more rapid transformations, and this has been possible by using specimens in the form of wires instead of blocks. The system lead-tin was chosen as it had previously been investigated kinetically (4), and the transformation velocity was known as a function of temperature and concentration.

§ 2. Experimental method

The alloys were made of analysed granular lead and tin from Baker's Chemical Co., N. Y., U. S. A. Analysis of the lead had given: Foreign N. V. M. 0.02%, As 0.00000%, Ag 0.000%, other foreign metals (as Fe) 0.001%. Analysis of the tin had given As 0.0000%, Cu 0.000%, Fe 0.003%, Pb 0.004%, Zn 0.000%.

First the granular metal was melted twice in an evacuated pyrex glass tube, and the oxid layer removed each time. Then the metals were melted together in vacuum, and the alloy was homogenized for ten hours at about twenty degrees below the solidus point. The loss in weight was always less than 0.02%. Thereupon it was rolled and drawn to a wire 0.7–1.6 mm in diameter. To check the homogeneity of the wires the resistance was measured in different parts by means of a Thomson double bridge, and if any difference of more than about 0.5% was found, the alloy was melted and homogenized again.

In Fig. 1 the main part of the measuring apparatus is shown. A cylindrical copper block 20 cm long and 4 cm in diameter was divided into two parts and formed according to the figure. The specimen wire *AB* was placed in the center of the copper block. Its ends were welded to copper wires fixed to one part of the block and insulated from this by mica. Two thin copper wires were soldered to the specimen wire at the points *C* and *D* and fixed to the same part of the copper block as the specimen. The alloy itself was used as solder. Thus it was possible to send an electric current through the specimen and other currents through the copper wires at *C* and *D*.

To measure the difference of temperature between the specimen and the copper block a series of constantan-manganin thermo-couples with a diameter of 0.07 mm was used. Every odd contact point was fastened to the specimen and every even one to the copper block. First the specimen wire was covered with a thin layer of silicon varnish, and the apparatus was placed in a thermostat at a temperature of about 150° C for 10–15 hours. Then it was possible to wind the thermocouples round the specimen in order to obtain good thermal contact and at the same time have electric insulation.

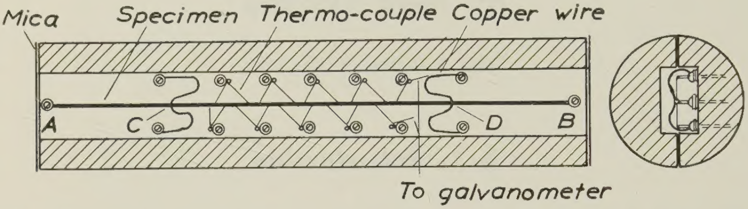

Fig. 1. Apparatus for calorimetric measurements during rapid transformations in alloys.

The even contact points were soldered to copper wires fixed with screws to the copper block and electrically insulated from this by mica. The specimen was then covered with a layer of silicon varnish again. There was some trouble in maintaining good electric insulation but it was not impossible. When after this treatment the apparatus had been heated to 100–150° C again, the thermo-couples adhered to the specimen, and it was possible to begin the measurements. The silicon varnish had also the advantage of protecting the specimen from oxidation. The apparatus described above was placed in a vapour thermostat with water or bromobenzene and well insulated outwards with cotton. For the measurements at 0° C an icebath was used, and for the three measurements at room temperature no thermostat at all was used but the copper block was well insulated. Of course these determinations were not as accurate as the others. The vapour thermostat is described in (1).

To homogenize the specimen electric currents were sent through it and through the crossing wires at *C* and *D*. To obtain the temperature of the specimen its electrical resistance was measured by means of an ammeter and voltmeter. As in the kinetic investigation of lead-tin alloys (4) it was sufficient to homogenize for one hour at 180° C, although the specimen in most cases was heated to this temperature for about 10 hours. In this investigation it was found that the heat produced is fairly independent of the time of homogenization, but the velocity of the transformation may depend on it. When the currents were cut off the specimen was cooled to the temperature of the thermostat, and the measurements of the evolution of heat could begin after one or two minutes. The EMF of the thermo-couples was measured by means of a mirror galvanometer as a function of time. When the transformation was slow enough, a current commutator was used to make measurements with the galvanometer in both directions. For very rapid transformations it was impossible to read the galvanometer deflections directly, and a simple recording apparatus constructed by JOHANSSON and LARRIS (5) was used.

In Fig. 2 some examples of curves of the galvanometer deflection are shown as a function of time. From the curve it is seen how the specimen at first attains the temperature of the thermostat. When the precipitation begins the temperature

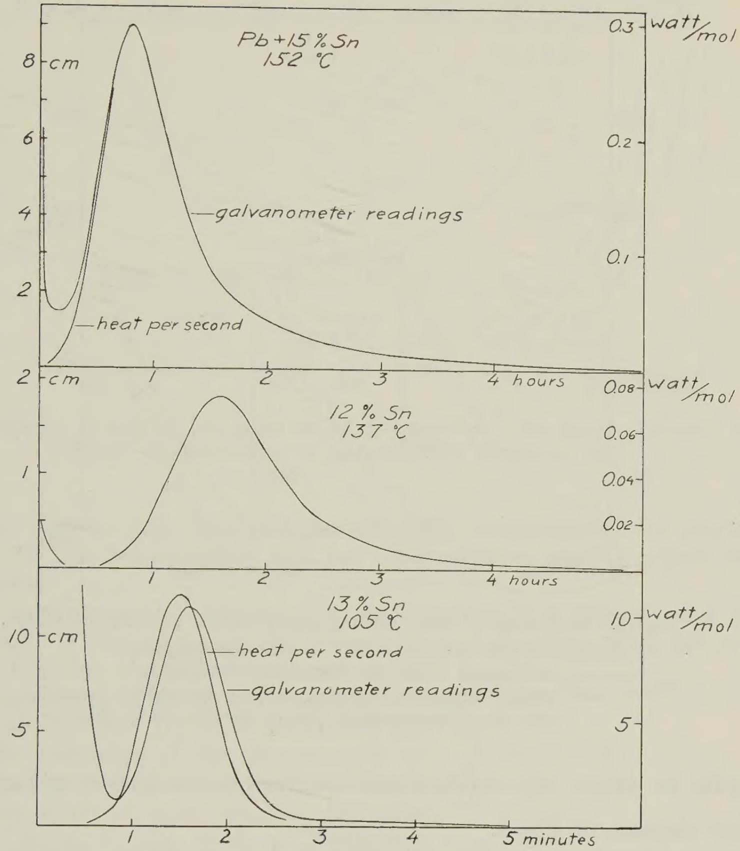

Fig. 2. Galvanometer deflection and heat per second as a function of time.

rises again, and from the difference of temperature between the specimen and copper block it is possible to calculate the heat produced.

To calibrate the apparatus a known electric current was sent through the specimen and the voltage was measured between the points C and D. As the weight of the specimen between these points was easy to calculate, the heat P per mol and second could be determined as a function of the galvanometer deflection s

$$P = A s + B \frac{d s}{d t}$$

where A was calculated from the equilibrium in the galvanometer deflection and B from the deflection change when the current was cut off. It is sometimes possible to omit $B \frac{d s}{d t}$ and the heat per second is proportional to the galvanometer deflection s if this varies slowly with time. In other cases with a large numerical value of $\frac{d s}{d t}$,

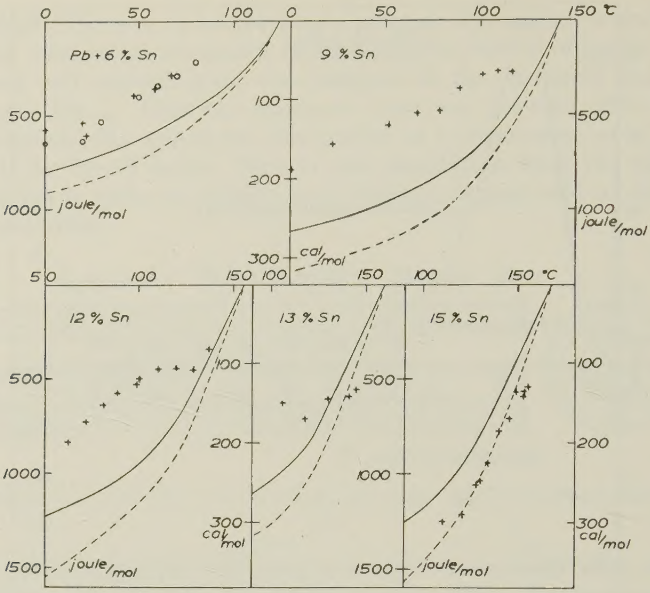

Fig. 3. Evolution of heat during precipitation in lead-tin alloys.
o Borelius and Säfsten (3) + this investigation
——— calculated from the two-phase boundary
- - - - - values obtained by means of a simplified formula and the experimental points for the 15 % alloy.

$B \frac{ds}{dt}$ must be taken into account and a correction has to be made as is shown in the third diagram of Fig. 2.

Sometimes, however, another correction had to be made. During homogenization of the specimen the copper block was also heated and reached a temperature a little different from the thermostat. Temperature gradients inside the copper block caused a galvanometer deflection, sometimes positive and sometimes negative. These deflections decreased as $e^{-\frac{t}{\tau}}$ where t is time and τ a constant (about 18 minutes). A correction of this kind is seen in the first diagram of Fig. 2. There was also in most cases an undesirable constant galvanometer deflection, which was dependent on the temperature of the thermostat and on how the copper block was placed in it.

§ 3. The experimental results

By integrating the curves in Fig. 2 it is possible to obtain the evolution of heat, and the results of these measurements are collected in Fig. 3 together with the results of an investigation of Borelius and Säfsten (3) made at the same time as this. Borelius and Säfsten used the same method as has been worked out earlier in this laboratory. As seen from the diagram the results of the two methods are in good agreement with each other. If the results are compared with the values calculated from the two-phase boundary according to Borelius (3) as will be described

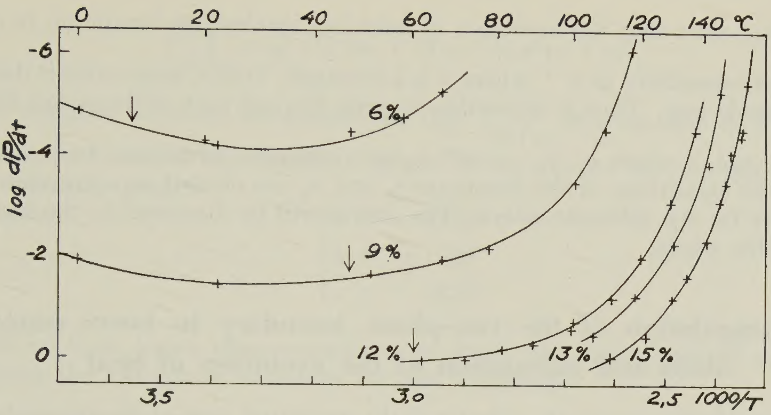

Fig. 4. Dependence of rate of precipitation on temperature. The arrows indicate the lower limits of retardation as calculated by BORELIUS (4).

in § 4, we see that for high temperatures and high concentrations we obtain larger values and for low temperatures and low concentration smaller values than the calculated ones.

From the experimental results of this investigation it is also possible to make kinetic studies. If the maximum increase of the calorimetric effect per second is plotted as a function of the inverse value of the absolute temperature (Fig. 4) as in the work of BORELIUS and SÄFSTEN (3) or if we choose the time from the beginning of the measurement to the moment when the maximum heat per second is evolved, we arrive at approximately the same result as is given in the work of BORELIUS, LARRIS and OLSSON (4). It is, however, possible to draw more conclusions from other details of the curves. As pointed out by BORELIUS (2) the form of the beginning of the power curves is very interesting. After a short time the heat produced per second increases along a straight line but this line does not point towards the origin of the diagram. If the logarithm of the heat per second is plotted as a function of the logarithm of time for the first part of the curve, it is seen that for low temperatures the power increases approximately as t^2 and for high temperatures as t^3. But these results are not quite certain, for the curve becomes a straight line after a very short time; for rapid transformations before the galvanometer deflection curve has reached its first minimum, and for very slow transformations before the galvanometer deflection has grown more than a few millimeters.

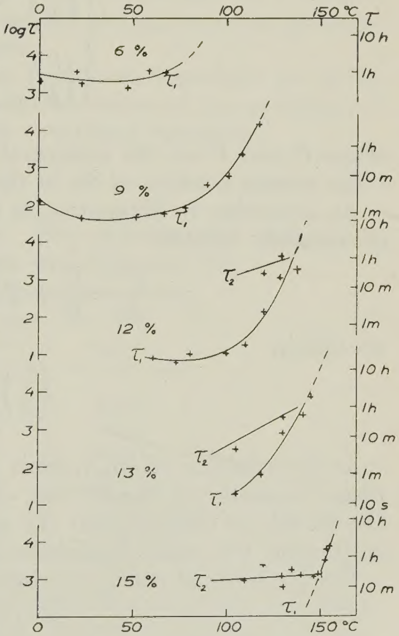

Fig. 5. The time constants τ as functions of temperature and concentration.

Some time after that the evolution of heat has reached its maximum it usually decreases exponentially as $e^{-\frac{t}{\tau}}$, where τ is a constant. But in some cases it decreases in a less simple way. Then it is possible to write the last part of the power function as $c_1 e^{-\frac{t}{\tau_1}} + c_2 e^{-\frac{t}{\tau_2}}$ where c_1, c_2, τ_1 and τ_2 are constants, which can be determined. In Fig. 5 the logarithms of the constants τ_1 and τ_2 are plotted as a function of the temperature for the different alloys. The curves will be discussed in the last paragraph of this paper.

§ 4. Extrapolation of the two-phase boundary to lower concentrations and calculation of the evolution of heat

Borelius (4) has previously calculated the structural part of the internal energy in lead-tin alloys. To calculate the evolution of heat at a certain temperature it is, however, also necessary to know the two-phase boundary for this temperature. But it is not possible to determine the two-phase boundary experimentally for lower concentrations than about 4% Sn, as the transformation in these cases is too slow. Therefore it must be calculated. For this purpose we introduce the molar structural free energy F_{Sn} for Sn in Pb alloys, and the molar structural internal energy U_{Sn}. These are defined by the equations

$$\begin{cases} \left(\frac{F}{R}\right)_{\mathrm{Sn}} = \frac{F}{R} + (1-x)\frac{d}{dx}\left(\frac{F}{R}\right) & (1) \\ \left(\frac{U}{R}\right)_{\mathrm{Sn}} = \frac{U}{R} + (1-x)\frac{d}{dx}\left(\frac{U}{R}\right) & (2) \end{cases}$$

where U and F are the structural parts of the internal energy and free energy and x the atomic fraction of Sn in the alloy.

As according to Borelius (6) the structural part of the free energy may be approximately written

$$\frac{F}{R} = \frac{U}{R} + T\left[x \ln x + (1-x)\ln(1-x)\right] \tag{3}$$

we obtain

$$\left(\frac{U}{R}\right)_{\mathrm{Sn}} = \left(\frac{F}{R}\right)_{\mathrm{Sn}} - T \ln x. \tag{4}$$

As the solubilty of Pb in Sn is very small we may approximate $(F)_{\mathrm{Sn}}$ for the two-phase boundary on the Pb-side with the free energy of the two-phase boundary on the Sn-side as calculated in (4), and U_{Sn} can be determined by Eq. (4) for the experimental two-phase boundary points.

For the internal energy we introduce the empirical formula

$$\frac{U}{R} = ax + bx^2 + cx^3 \tag{5}$$

where a, b and c are constants and obtain

$$\left(\frac{U}{R}\right)_{\mathrm{Sn}} = a + 2\,b\,x + (3\,c - b)\,x^2 - 2\,c\,x^3. \tag{6}$$

The constants are then determined so that $\left(\frac{U}{R}\right)_{\mathrm{Sn}}$ as a function of x is in good agreement with values calculated by means of Eq. (4) for the experimental two-phase boundary points.

We obtain

$$\begin{cases} a = +\,1235^\circ \\ b = -\,1930^\circ \\ c = +\,1420^\circ \end{cases}$$

When we have found these constants, we know the molar internal energy and can obtain the two-phase boundary for low values of x.

$\left(\frac{F}{R}\right)_{\mathrm{Sn}}$ for the two-phase boundary is almost the same as the free energy for the boundary on the Sn-side at the same temperature and may be neglected when compared with U_{Sn} in Eq. (4) and x for the two-phase boundary can be obtained from the intersections between the curves of $\frac{1}{T}\left(\frac{U}{R}\right)_{\mathrm{Sn}}$ and $\ln x$ as functions of the concentration x for fixed values of the absolute temperature T.

The values of the internal energy from Eq. (5) are in good agreement with those calculated by BORELIUS (4). As the two-phase boundary and the internal energy are known as functions of the concentration, it is easy to calculate the evolution of heat as the difference between the internal energy of the super-cooled homogeneous phase and that of the two new stable phases.

The experimental and calculated values for the two-phase boundary are given in Table 1. The fully drawn lines in Fig. 3 represent the values of the evolution of heat for the different alloys as calculated from the two-phase boundary.

Table 1

The two-phase boundary for lead-tin alloys. The experimental values are determined by BORELIUS, LARRIS and OHLSSON (4)

Atomic fraction of Sn	t (°C) calc.	Atomic fraction of Sn	t (°C) exper.
0.013	0	0.076	109.5
0.020	25	0.100	123.5
0.030	50	0.147	141.5
0.045	75	0.192	155.5
0.068	100	0.236	168.5
		0.277	182.5
		0.9855	183

We may assume that for high temperatures and high concentrations we obtain from our measurements all the heat of precipitation. But for the lower concentrations the precipitation is not completed during the time of the calorimetric measurements. The first part of the precipitation comes rapidly, but internal stresses prevent complete precipitation (3).

To compare the heat evolved for low concentrations with that for high concentrations, the dotted lines in Fig. 3 are drawn. Those lines represent values calculated for the evolution of heat by means of the same two-phase boundary as previously and the following simplified formula for the structural part of the internal energy,

$$\frac{U}{R} = 1380\, x\,(1 - x) \tag{7}$$

where the constant 1380 has been determined from the evolution of heat for the 15% alloy.

Formula (7) can be obtained from the theory of the energy of nearest neighbours according to BETHE (7).

As seen from the figure about half of the total amount of heat is evolved for low temperatures.

The difference between the experimentally measured evolution of heat and the values calculated from the two-phase boundary may be explained in the following way. These calculations are approximate since no consideration has been taken of deviations from the law of KOPP-NEUMANN, which assumes a rectilinear dependence of the specific heat upon the atomic concentration of the alloy. As the lattice of tin-rich alloys is different from that of the lead-rich alloys investigated, it is very probable that the specific heat of these different parts of the system are different linear functions of the concentration.

§ 5. Discussion of the transformation velocity and the form of the power curves

If Fig. 5 is studied, it is easy to see that precipitation comes in two stages. For the alloy with 6 and 9% Sn the second stage is too slow to be detected during the measurements and only half of the total energy is evolved. For the alloys with 12 and 13% Sn both stages are rapid enough to be detected by means of the calorimetric measurements. For the alloys with 15% Sn we see that below 150° the time τ varies very little with the temperature but for higher temperatures it increases very rapidly. If the curve is compared with the curves for the other concentrations, we may assume that the measured time τ is fixed by the second stage of precipitation below 150° and by the first stage of precipitation above 150°. The first stage is too rapid for measurements below this temperature.

This fact may be explained in the following way. The first stage of the transformation is a formation of nuclei which grow to a precipitate later. Sometimes knots or clusters are formed within the old matrix according to GUINIER (8) and PRESTON (9), but in that case the evolution of heat would probably have decreased as a hyperbolic function as shown by BORELIUS and collaborators (1) and not as $e^{-\frac{t}{\tau}}$ as in this investigation. For low temperatures only diffusion difficulties limit the transformation velocity, and for formation of nuclei the distance of diffusion for the atoms is much shorter than that for precipitation. So the time τ_1 becomes much shorter than τ_2. But in a temperature range just below the two-phase boundary, formation of knots is hindered by a potential barrier, as pointed out by BORELIUS (4, 10), and the time τ_1 increases very rapidly with the temperature. For the 15% alloy the time τ_1 becomes larger than τ_2 at 150° C and for higher temperatures τ_1 alone determines the rate of precipitation.

Like BORELIUS (2) we assume that the heat evolved per second may be written

$$P = n \cdot \bar{q}$$

where n is the number of clusters of tin atoms per mol of the alloy and $\bar{q}$ the mean value of the heat produced by each cluster. In the beginning of the precipitation n is zero, it then increases with a characteristic velocity and becomes proportional to the time.

$$n = k_1 \cdot t.$$

If the clusters grow in only one direction, $\bar{q}$ is constant and P becomes proportional to the time.

If the clusters grow in two dimensions $\bar{q}$ becomes proportional to the radius, that is to the age of the cluster. As the mean value of the age is $\frac{t}{2}$ we can write

$$\bar{q} = k_2 \cdot t$$

and

$$P = k_3 \cdot t^2$$

for small values of t, where k_1, k_2 and k_3 are constants. As mentioned in § 3 it is probable that the heat evolved increases in this way for low temperatures.

If the clusters grow in three dimensions $\bar{q}$ becomes proportional to the mean value of their surface area, which is proportional to the square of their linear dimensions or to t^2

$$\bar{q} = k_4 t^2$$

$$P = k_5 t^3.$$

As our experiments show this is probably true for high temperatures and high concentrations.

This investigation has been carried out at the Physical Department of the Royal Institute of Technology in Stockholm, and the author wishes to express his gratitude to the Director of the Department Professor G. BORELIUS for his great interest in the work and for much valuable discussion.

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